Modeling Bleaching of Tomato Derivatives at Subzero Temperatures

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This work was addressed to obtain a predictive model of the rate of bleaching in tomato derivatives at subzero temperatures. To this aim, a tomato puree was freeze-dried and equilibrated at increasing solid fractions. The bleaching rate was assessed by measuring tomato color during storage for up to 18 months at temperatures from −30 to 0 °C. The temperature dependence of the tomato-bleaching rate was neither predictable using the Arrhenius equation nor simply related to tomato physical state. The lack of a clear Arrhenius relation was attributed to the occurrence of temperature-dependent phenomena, such as ice crystallization and oxygen solubility modifications, which strongly changed the local concentration of reactants. A modified Arrhenius equation predicting the tomato-bleaching rate in the entire temperature range was proposed. Tomato concentration, and hence its physical state, affected the temperature dependence of bleaching, modifying apparent activation energy and frequency factor of the modified Arrhenius equation. In light of these considerations, a mathematical model was set up and validated to accurately predict the tomato-bleaching rate on the basis of only its concentration and storage temperature.

INTRODUCTION

Simple methodologies are available to directly measure the shelf life of perishable foods. Unfortunately, they do not help when dealing with relatively stable foods with a medium-long shelf life. The direct measurement of their shelf life is slow and definitely not consistent with the short life span of products in competitive markets. For this reason, the prediction of the shelf life of foods during their development process is highly suggested, thereby enabling technological remedies to be applied. It is important that such prediction methods be effective enough to evaluate even slow rates of degradation, yet remain accurate.

The accurate prediction of long-term stability is actually dependent on the availability of an accurate kinetic model of the phenomena leading to quality depletion during food storage. Traditionally, it is convenient to accelerate shelf life experiments by testing food under environmental conditions that speed up food quality depletion and then extrapolating the results to milder conditions usually experienced by the product (*1−3*). Despite many accelerating environmental factors (temperature, relative humidity, pressure, and light, among others) that are known, temperature is often the only one commonly exploited in accelerated shelf life testing (ASLT). This is due to the availability of a theoretical basis, described by the Arrhenius eq 1, for the development of a mathematical description of the temperature sensitivity of the product (*4*):

$$k = k_{o} \cdot e^{-E_{a}/RT} \qquad (1)$$

where k is the reaction rate constant, R is the molar gas constant (8.31 J/K/mol), T is the absolute temperature (K), E_{a} is the activation energy (J/mol), and k_{o} is the frequency factor. While E_{a} is well-known to be the minimum energy allowing molecules to get close enough to cause a specific rearrangement of bonds, k_{o} depends on the chance that the molecules will collide in the correct orientation for rearrangement (*5*).

Because of the complexity of food systems, ASLT requires a wide amount of data relevant to the reaction rate as a function of temperature to be collected and fitted. Besides its demand on facilities and skills, this process is fraught with the risk of large deviations from predicted behavior (*6−10*). It may often happen that the model correctly predicts data in a typical portion of the region of interest but significant deviations are observed at the boundaries. As reviewed by Waterman and Adami (*11*), the major reasons for nonlinearity in Arrhenius plots are as follows: phase transitions, pH shifts, solubility changes, uncontrolled relative humidity, complex reaction mechanisms, and heat capacity changes of the activated complex.

Prediction errors can occur because the model is not of the correct functional form or merely because factors considered by the model are not those actually influencing food stability (*12*). If the latter causes the model failure, dominant factors, which control rate responses, should be identified and a new kinetic theory has to be developed. A famous example is that of the William−Landel−Ferry (WLF) model, based on viscosity properties of the system near glass transition temperature (*13*).

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Bleaching of Tomato Derivatives at Subzero Temperatures

J. Agric. Food Chem., Vol. 54, No. 4, 2006 **1303**

In other cases, the Arrhenius model is still useful but requires some modification or rescaling of model variables (*14, 15*). To take into account the nonlinear Arrhenius behavior, it is possible to use modified Arrhenius relationships, such as that reported by IUPAC (*16*):

$$k = A \, T^n \, e^{-E_a/RT} \tag{2}$$

Here, A, n, and E_a are parameters determined using nonlinear fitting programs (*11*). The use of these equations allows for a better mathematical description of some level of the curvature in Arrhenius plot, but parameters are pure corrective factors with no specific relation to phenomena causing deviation. In other words, they are empirical equations without mechanistic implications, unless the physicochemical meaning of parameters is identified.

The factor T^n could indicate that, in a certain region, the dominant factor affecting reaction rate (i.e., temperature) may alter the local status of the system. For instance, temperature is well-known to modify the physical state and the physicochemical properties of components (e.g., pressure, solubility, and diffusivity) leading to a modification of the local concentration of reactants. In a previous paper, we modified the Arrhenius equation in order to model non-Arrhenius behavior of lipid oxidation in frozen foods (*10*). An accurate predictive model was achieved by introducing oil liquid fraction and viscosity as additional factors.

This time, we address the bleaching of pigments, which is well-known to be a major cause of product quality depletion below acceptable limits for shelf life (*17−24*). Despite the fact that temperature is recognized as one of the main factors affecting color fading of pigments, the rate of these reactions is not simply predictable using traditional models such as Arrhenius or WLF (*25*). The lack of a clear mathematical model hinders the possibility to correctly estimate the shelf life of pigment-containing foods.

On the basis of these considerations, the aim of the present work was to find a reliable predictive model to assist in shelf life decisions relevant to foods where pigment bleaching is the prevalent event leading to quality depletion. To this purpose, tomato products were chosen as typical examples of pigment-rich foods (e.g., carotenoids and anthocyanins) (*26−30*). To study tomato bleaching in a wide range of derivatives, a tomato puree was freeze-dried and equilibrated at increasing solid weight fractions from 0.06 to 0.99 g_{dm} g^{-1}. In this way, samples representative of different tomato products (e.g., freeze-dried, double and triple strength pastes, and puree) and characterized by different physical states were obtained from the same tomato matrix. Color bleaching was assessed during storage for up to 18 months at temperatures ranging from −30 to 0 °C. This temperature range was selected in order to study the effect of pigment bleaching only, preventing color changes due to the occurrence of nonenzymatic browning.

MATERIALS AND METHODS

Sample Preparation. A commercial pasteurized tomato puree was freeze-dried (Mini Fast model 1700, Edwards Alto Vuoto Spa, Milano, Italy) and equilibrated at different a_w values in order to obtain samples with different solid weight fractions. In particular, 6 cm diameter Petri dishes containing approximately 1 g of dried tomato puree were placed in vacuum desiccators containing saturated salt solutions (Carlo Erba, Milano, Italy), with equilibrium relative humidity values up to 99%, and maintained at 25 °C. Samples with decreasing tomato solid fraction (g_{dm} g^{-1}) were thus obtained (**Table 1**).

Table 1. Water Activity (a_w), Glass Transition Temperature (T_g), and Ice Melting Temperature (T_m) of Tomato Puree with Increasing Solid Fraction

solid fraction	a_w	T_g (°C)	T_m (°C)
0.00	1.00	−136.0	0.00
0.06	0.99		−14.1
0.16	0.97		−27.8
0.44	0.91		−47.3
0.59	0.84	−88.2[a]	
0.62	0.81	−83.9	
0.71	0.75	−68.9	
0.78	0.68	−58.3	
0.87	0.52	−33.0	
0.94	0.33	−10.4	
0.96	0.25	1.4	
0.97	0.21	5.7	
0.99	0.12	17.2	

[a] T_g of the maximally freeze-concentrated sample.

Sorption isotherms were obtained by carefully weighting samples when equilibrium conditions were reached. Petri dishes containing samples with different solid weight fractions were then sealed and stored for up to 18 months at −30, −18, −7, and 0 °C.

Calorimetric Analysis. Calorimetric analyses were made by means of a TA 4000 differential scanning calorimeter (Mettler Toledo, Greifensee, Switzerland) equipped with a DSC 30 low-temperature measuring cell and a TC11 TA processor connected to a Graph Ware software (TA 72.2/0.5, Switzerland). Heat flow was calibrated using indium (heat of fusion, 28.45 J/g). Temperature was calibrated with *n*-butyl alcohol (mp −89.5 °C), water (mp 0 °C), and indium (mp 156.6 °C). Amounts of about 5 mg of tomato sample, exactly weighed, were placed in 40 μL capacity aluminum pans. An empty aluminum pan was used as a reference. Samples were heated from −150 to 250 °C at 10 °C min^{-1}. Thermograms were analyzed for the onset temperatures of glass transition (T_g) and ice melting (T_m) (**Table 1**).

The T_g curve was best fit ($R^2 = 0.98$, $p < 10^{-3}$) by the Gordon and Taylor (1952) relation with the empirical k constant assuming a value of 0.3072:

$$T_g = \frac{-136(1 - C_o) + kC_o T_{gdry}}{(1 - C_o) + kC_o} \tag{3}$$

where C_o is the tomato solid fraction (g_{dm} g^{-1}) and T_{gdry} is the T_g of the freeze-dried tomato (20 °C).

The melting temperature (T_m) of tomato at solid fraction up to 0.4 was well-described ($R^2 = 0.98$, $p < 10^{-3}$) by the equation:

$$T_m = -115.35 C_o \tag{4}$$

The enthalpy value of ice melting (ΔH_m) was obtained by integration of the melting peak. The amount of frozen water was calculated as the ratio between ΔH_m and the enthalpy of pure ice melting (333.5 J/g). From the value of unfrozen water, the solid fraction of the maximally freeze-concentrated solution ($C_g' = 0.59$) was calculated.

At each temperature below freezing, the freeze concentration factor (C) of the unfrozen aqueous phase was defined as the ratio between the solid fraction of the unfrozen solution in contact with ice (C_g) and the solid fraction originally present in the sample above the freezing temperature (C_o):

$$C = \frac{C_g}{C_o} \tag{5}$$

Oxygen Solubility. The oxygen solubility in water below zero was calculated by using the following equation:

$$\ln X = a + \frac{b}{T^*} + c \ln T^* \tag{6}$$

1304 *J. Agric. Food Chem.,* Vol. 54, No. 4, 2006

Manzocco et al.

Table 2. Solid Fraction of Tomato Puree Corresponding to the Physical State of (i) Concentrated Solution in Contact with Ice, (ii) Solution, and (iii) Glass as a Function of Temperature

temp (°C)	concentrated solution + ice	solution	glass
0		<0.97	>0.97
−7	<0.06	>0.06, <0.94	>0.94
−18	<0.16	>0.16, <0.91	>0.91
−30	<0.26	>0.26, <0.87	>0.87

(header: solid fraction)

where X is the molar fraction of oxygen in water; T^* is the temperature in Kelvin multiplied for 10^{-2}; and a, b, and c are equation constants, which are −66.7354, 87.4755, and 24.4526, respectively (*31*).

At each temperature, the oxygen solubility factor (O) was defined as the ratio between oxygen solubility at temperature T (O_T) and oxygen solubility at 0 °C (O_o):

$$O = \frac{O_T}{O_o} \qquad (7)$$

Color. Changes in tomato color were assessed by a tristimulus colorimeter (Chomameter-2 Reflectance, Minolta, Osaka, Japan) equipped with a CR-200 measuring head. The instrument was standardized against a white tile. Color was expressed in L^*, a^*, and b^* Hunter parameters.

Pigment Bleaching Rate. Pigment bleaching was measured by following the changes in the ratio of the Hunter color parameters $b^* a^{*-1}$ of tomato. Bleaching was actually observed to follow the zero-order kinetic, and apparent bleaching rates (k) were calculated by linear regression of $b^* a^{*-1}$ as a function of storage time, excluding the eventual lag phase.

The effect of temperature on k was evaluated by means of the Arrhenius eq 1. To better estimate the apparent activation energy (E_a) and frequency factor (k_o), the following reparametrized Arrhenius equation was used

$$k = k_{ref} \, e^{-E_a/R(1/T - 1/T_{ref})} \qquad (8)$$

where k is the apparent bleaching rate, R is the molar gas constant (8.31 J/K/mol), T is the absolute temperature (K), and k_{ref} is the apparent bleaching rate at T_{ref} (*11, 32*). T_{ref} was chosen as 258 K, which is the central value of the temperature interval considered in the study. The apparent activation energy E_a and k_{ref} were determined by linear regression analysis and used to calculate k_o:

$$k_o = e^{(\ln k_{ref} + E_a/RT)} \qquad (9)$$

Data Analysis. The results reported in this work are the averages of at least three measurements taken from different samples, and the coefficients of variation, expressed as the percentage ratio between the standard deviation and the mean value, were found to be <3% for color and a_w, <4% for T_g and T_m, and <10% for k_{ox}. Least squares linear regression analysis was performed by using Statistica for Windows (version 5.1, Statsoft Inc., Tulsa, OK). Best fitting analysis was performed by using Table Curve 2D for Windows (version 4, SPPS Inc., Chicago, IL).

RESULTS AND DISCUSSION

Physical and Chemicophysical Properties of Tomato. Depending on solid fraction and storage temperature, tomato puree was characterized by different physical states, as shown in **Table 2**. In the temperature range selected in this research to investigate pigment bleaching (from −30 to 0 °C), three different physical situations were achievable as follows: (i) glassy tomato puree, (ii) tomato puree as an aqueous solution, and (iii) tomato puree as a freeze-concentrated solution in contact with ice.

Table 3. Concentration Factor (*C*) of Tomato Samples with Different Solid Fraction (C_o) as a Function of Temperature

| temp (°C)	$C_o = 0.06$	$C_o = 0.16$	$C_o > 0.16$
0	1	1	1
−7	1	1	1
−18	2.6	1	1
−30	5.8	2.2	1

(header: concentration factor (C))
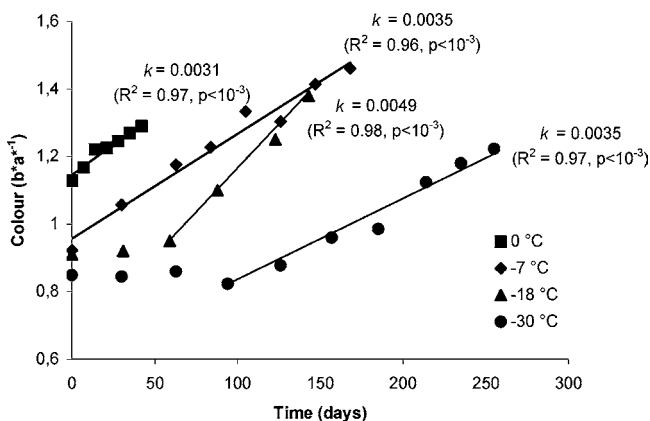
Figure 1. Color ($b^* a^{*-1}$) of tomato puree with 0.94 solid fraction as a function of storage time at −30, −18, −7, and 0 °C. The apparent zero-order rate constants of pigment bleaching (k) and the relevant statistical parameters are also shown.

It can be noted that at low solid weight fraction, ice formation occurred leading to the concentration of tomato solids in the unfrozen aqueous solution. The amount of ice in these samples was assessed by calorimetric analysis and used to calculate the concentration of the unfrozen solution. The concentration factor (*C*) was thus defined according to eq 5. *C* values, reported in **Table 3**, indicate how many times the tomato concentration was increased as a consequence of freezing. A *C* value equal to 1 indicates that, at the given temperature, freezing did not occur and the sample concentration remained unchanged. By contrast, *C* values higher than 1 indicate that water is partially frozen at the given temperature leading to a *C*-times increase in the concentration of the unfrozen solution. For instance, a sample with initial 0.06 solid fraction froze at −7 °C (eq 4) and its concentration (C_g) at −18 and −30 °C became, respectively, 2.6 and 5.8 times the initial concentration (C_o).

Tomato Bleaching. Tomato samples with different solid fractions were stored for increasing times at different temperatures and assessed for color. To study the effect of only pigment bleaching, samples were stored at temperatures ranging from −30 to 0 °C. At these temperatures, pigment bleaching is mainly attributable to the development of oxidative reaction of pigments (e.g., carotenoids) and can be regarded as the prevalent reaction leading to changes in tomato color. Storage temperatures higher than 0 °C were thus not considered because of the possible development of nonenzymatic browning, which could eventually mask color changes due to pigment bleaching.

The changes in the color parameter ratio $b^* a^{*-1}$ of tomato with 0.94 solid fraction are shown, as examples, in **Figure 1**. The increase in the $b^* a^{*-1}$ ratio indicated the progressive bleaching of tomato, which turned its color from red to yellow. However, it must be noted that at −18 and −30 °C, a lag phase, whose duration was longer as temperature decreased, was observed. To calculate bleaching rates (k, $b^* a^{*-1}$ day^{-1}), linear regression analysis was performed according to the zero-order equation, excluding the eventual lag phase.

Bleaching of Tomato Derivatives at Subzero Temperatures

*J. Agric. Food Chem.,* Vol. 54, No. 4, 2006 **1305**
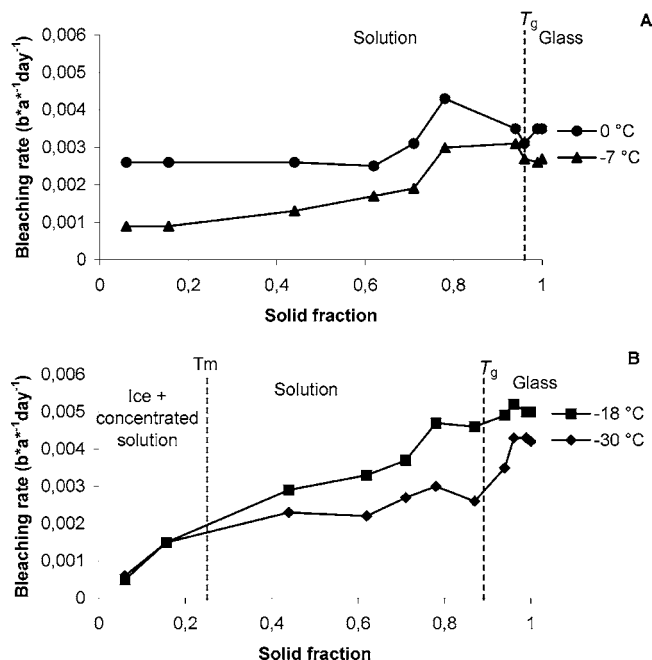
Figure 2. Apparent zero-order rate constants of tomato bleaching as a function of solid fraction of tomato puree stored at 0 and −7 °C (**A**) and −18 and −30 °C (**B**).

Figure 3. Apparent zero-order rate constants of tomato bleaching with different solid fraction as a function of temperature.

The values of k ($R^2 > 0.95$, $p < 10^{-2}$) relevant to tomato with increasing concentrations stored in the temperature range from 0 to −30 °C are shown in **Figure 2**. By analyzing the evolution of k (**Figure 2**) and taking into account the physical state of tomato puree (**Table 2**), it can be observed that bleaching quickly proceeded even in the glassy state. In particular, at −30 and −18 °C, the highest k values were observed when tomato was in the glassy state. It has been suggested that deteriorative changes at reduced a_w depend on molecular mobility, which is governed by the physical state of food solids (*33, 34*). The high k observed in glassy tomato clearly indicates that pigment oxidation is not a diffusion-limited reaction since oxygen, by virtue of its small molecular weight, can freely diffuse and react with pigments even in a glassy matrix. In other words, storage below glass transition temperature does not allow pigment stability to be obtained, and neither is it a sufficient condition to slow down the reaction.

Below glass transition, two different evolutions were observed depending on storage temperature. In fact, as T_g was overcome, samples stored at −30 and −18 °C were characterized by a progressive decrease in bleaching rate. By contrast, at −7 and 0 °C, a maximum in bleaching rate, whose intensity increased with temperature, was observed at ca. 0.8 solid fraction.

These results confirm that the effect of tomato solid fraction on pigment bleaching is strongly dependent on storage temperature. To further investigate the critical effect of temperature, k values were plotted according to the Arrhenius model (**Figure 3**).

Unexpectedly, the decrease in storage temperature was not always associated to an increase in color stability. In fact, an Arrhenius type relation between bleaching and temperature was not achieved. Although proceeding at a considerably high rate, bleaching was not significantly affected by temperature in tomato samples with solid fractions higher than 0.62. In these conditions, bleaching proceeded at similar magnitude rates in the entire temperature range. This result confirms that below glass transition (e.g., sample with 0.99 solid fraction), reactions generally proceed independently of temperature. However, the
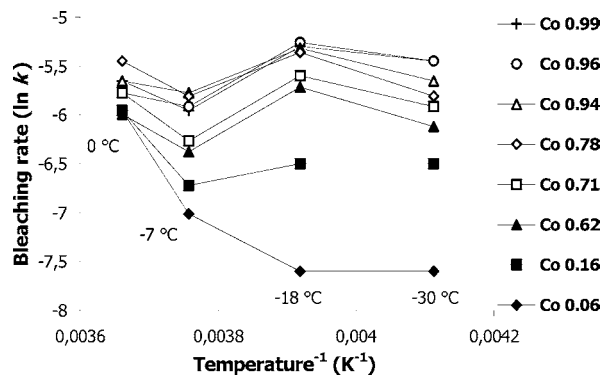
lack of a clear Arrhenius type relation in tomato samples with a solid fraction corresponding to the physical state of a solution ($0.62 < C_o < 0.99$; **Table 2**) suggests that factors other than temperature, such as the increase in oxygen solubility, may counterbalance the reduction in k expected on the basis of the sole temperature decrease.

Samples with solid fraction below 0.62 presented more complex behaviors. For instance, at 0.06 solid fraction, the decrease in temperature was associated to an initial decrease in k, which was followed by an abrupt change in k temperature dependence at −18 °C. It is interesting to note that this sample was a solution only at a temperature higher than −10.4 °C (eq 4). Below this temperature, water partially froze and reactants were concentrated in the unfrozen solution. A similar behavior was also observed for tomato samples with an initial solid fraction of 0.16, which presented a freezing temperature of −16.5 °C.

Tomato Bleaching Model. Data shown in **Figure 3** clearly indicate that the bleaching rate in tomato is not simply predictable using the Arrhenius model. As known, the lack of a clear Arrhenius relation often happens when temperature-dependent phenomena (e.g., phase transitions, solute concentration, and changes in physicochemical properties) occur (*8, 35*).

It can be hypothesised that storage temperature exerts not only a direct effect on pigment bleaching but also an indirect effect by changing the local concentration of reactants. It must be noted that tomato bleaching can be attributed to the development of oxidative reactions of pigments, mainly carotenoids. Because the latter are well-known to be oxygen quenchers, the main reactants leading to tomato bleaching can be hypothesised to be carotenoids and oxygen. This hypothesis is confirmed by the evidence that pigment bleaching was actually not observed when tomato samples were stored under vacuum (data not shown), indicating that significant changes in tomato color necessarily require the presence of molecular oxygen to occur.

For these reasons, while temperature can be regarded as an independent variable, the local concentration of reactants (i.e., carotenoids and oxygen) is strongly temperature-dependent. In fact, despite being affected by the initial solid fraction of tomato sample, pigment local concentration is expected to increase as the temperature is lowered below the freezing point (**Table 2**). Similarly, oxygen concentration in the aqueous solution is well-known to increase as temperature decreases. Oxygen solubility data were used according to eq 6 to calculate the oxygen solubility factor (O) defined as the ratio between oxygen solubility at temperature T (O_T) and oxygen solubility at 0 °C (O_o). Similarly to the concentration factor (C), the oxygen solubility factor indicates how many times the oxygen concen-

1306 *J. Agric. Food Chem.,* Vol. 54, No. 4, 2006

Manzocco et al.

Table 4. Oxygen Solubility Factor (O) in Aqueous Media as a Function of Temperature

temp (°C)	oxygen solubility factor (O)
0	1
−7	1.19
−18	1.59
−30	2.10
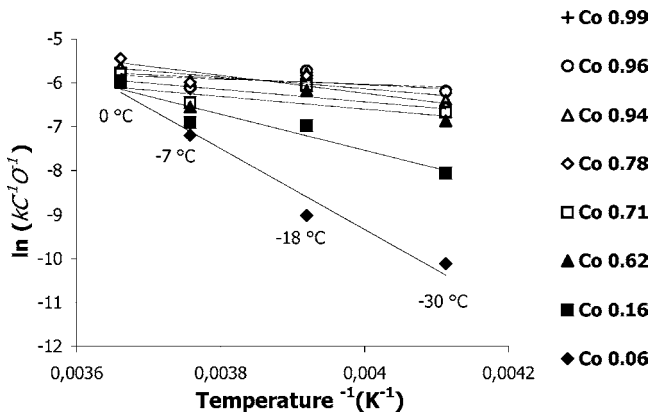
Figure 4. Apparent zero-order rate constants of bleaching, expressed as $\ln(k \cdot C^{-1} \cdot O^{-1})$ in tomato with different solid fraction as a function of temperature. Lines were obtained by regression analysis according to eq 12.

tration in tomato puree is increased as a consequence of the temperature decrease. Despite being calculated on the basis of estimated solubility and not accounting for the solute effect, oxygen solubility factors shown in **Table 4** indicate that the oxygen concentration at −30 °C is likely to be more than twice as that measured at 0 °C.

On the basis of these considerations and according to eq 2, a modified Arrhenius equation accounting for temperature and other factors affecting pigment bleaching in tomato was proposed

$$k = \Delta k \cdot k_o \cdot e^{-E_a/RT} \tag{10}$$

where k is the bleaching rate, R is the molar gas constant (8.31 J/K/mol), T is the absolute temperature (K), E_a is the activation energy (J/mol), k_o is the frequency factor, and Δk is a corrective factor, which takes into account the main factors involved in the Arrhenius deviations.

At a given temperature, the rate at which any reaction develops is the result of the ratio between driving forces and resistances (*10*). Although no significant resistances were identified, the main driving forces besides temperature were considered to be the concentration of pigments upon freezing and the increase in oxygen solubility. The corrective factor Δk in eq 10 was thus substituted by the product of concentration factor (C; **Table 3**) and oxygen solubility factor (O; **Table 4**):

$$\Delta k = C \cdot O \tag{11}$$

Substituting eq 11 in eq 10, the model proposed becomes

$$k \cdot C^{-1} \cdot O^{-1} = k_o \cdot e^{-E_a/RT} \tag{12}$$

The new dependent variable $k \cdot C^{-1} \cdot O^{-1}$, generated considering the effect of temperature and reactants' concentration, is shown in **Figure 4**. It must be noted that the temperature dependence of the variable $k \cdot C^{-1} \cdot O^{-1}$ was strongly affected by the initial

Table 5. Apparent Activation Energy (E_a) and Frequency Factor (k_o) as a Function of Tomato Solid Fraction[a]

solid fraction	E_a (kJ/mol)	k_o	r	SE
0.06	105.64	5.01×10^{17}	0.99	0.00001
0.16	44.37	6.80×10^5	0.93	0.00030
0.62	11.39	0.34	0.71	0.00030
0.71	12.53	0.65	0.71	0.00037
0.78	16.66	6.16	0.86	0.00041
0.94	10.07	0.28	0.81	0.00029
0.96	4.26	0.01	0.45	0.00033
0.99	6.51	0.05	0.57	0.00037

[a] Statistical parameters of regression according to reparametrized eq 12 are also reported.

solid fraction of tomato sample. Regression analysis of $k \cdot C^{-1} \cdot O^{-1}$ vs temperature was performed for each tomato concentration according to reparametrized eq 12 (T_{ref} equal to 258 K). Parameters of regression were used to calculate apparent activation energy and k_o for each tomato concentration (**Table 5**).

The statistical parameters of regression were observed to get worse as the tomato solid weight fraction increased. The apparent activation energy decreased concomitantly. In particular, tomato samples with solid fractions higher than 0.94, which were glassy in the entire temperature range (**Table 2**), exerted very low E_a values with unsatisfactory statistical parameters of regression. The decrease in k_o with the increase in solid fraction suggests that the number of successful collisions between reactants is lower in concentrated systems (*5*). These results confirm that the bleaching rate is reasonably independent of temperature in glassy tomato but dramatically susceptible to temperature changes when tomato is a solution or a freeze-concentrated system. In other words, the physical state is likely to affect the temperature sensitivity of tomato, changing the apparent activation energy and frequency factor in the modified Arrhenius equation (eq 12). Although the values of Arrhenius parameters are generally assumed to be constant for a given reaction, significant changes in the heat capacity of the activated complex are reasonably expected as a consequence of the modification of the physical state of the reactants (*11, 35, 36*).

It must be noted that the reaction between pigments and oxygen may occur in different physical phases according to the solid fraction of tomato. In fact, in concentrated systems, oxygen in the gas phase is likely to directly react with pigments, which are embedded in a glassy tomato matrix. In these conditions, the number of successful collisions between pigments and oxygen is low and the reaction proceeds at a rate that is almost independent of temperature. By contrast, in diluted systems, pigments are oxidized by oxygen solubilized in the aqueous phase. Because of the high molecular mobility, the number of collisions is expected to be lower than that with molecular oxygen. In addition, because the E_a is higher, only a limited part of the collisions has enough energy to make the reaction occur. The reaction rate is thus slower and strongly temperature-dependent.

Examining data presented in **Table 5**, it can be noted that the activation energy changed when 0.62 solid fraction was overcome. This value is much higher than that relevant to the formation of the monolayer calculated according to BET eq 37. It can be hypothesised that the water content corresponding to the monolayer is not sufficient to modify the physical environment in which molecular oxygen reacts. In other words, much more water is necessary to make the reaction prevalently occur with oxygen dissolved in the aqueous media. This is probably

Bleaching of Tomato Derivatives at Subzero Temperatures

J. Agric. Food Chem., Vol. 54, No. 4, 2006 **1307**

Table 6. Regression Coefficient ($R^2 = 0.99$, $P < 0.01$) of Apparent Activation Energy (E_a) and Frequency Factor (k_o) as a Function of Tomato Solid Fraction According to Eq 13

	regression results		regression results
f_{E_a}	−0.257	$f_{\ln k_o}$	−5.826
g_{E_a}	8.641	$g_{\ln k_o}$	3.603
h_{E_a}	−0.890	$h_{\ln k_o}$	−0.909

Table 7. Experimental and Predicted Values of Apparent Zero-Order Rate Constants of Bleaching in Tomato with 0.44 Solid Fraction as a Function of Temperature

	bleaching rate ($b^*\, a^{*-1}\,\mathrm{day}^{-1}$)	
temp (°C)	experimental	predicted by eq 14
−30	0.0023	0.0020
−18	0.0025	0.0022
−7	0.0017	0.0023
0	0.0026	0.0024

the reason a simple mathematical relation between Arrhenius parameters (E_a and k_o) and water activity of the sample was not achieved. By contrast, best fitting analysis allowed identifying a simple descriptive equation of E_a and k_o as a function of initial tomato solid fraction (C_o). The data were well-described by a power law equation:

$$y = f + g \cdot C_o^h \qquad (13)$$

where y is the apparent activation energy (E_a, kJ/mol) or $\ln k_o$, C_o is the initial tomato solid fraction, and f, g, and h are regression coefficients (**Table 6**).

Substituting eq 13 and relevant regression coefficients (**Table 6**) in eq 12, a general model for bleaching rate in tomato can be achieved

$$k = C \cdot O \cdot e^{[f_{\ln ko} + g_{\ln ko} \cdot C_o^h \ln k_o - (f_{E_a} + g_{E_a} \cdot C_o^h E_a)/RT]} \qquad (14)$$

Because oxygen and pigment concentration are temperature-dependent parameters, eq 14 actually represents a predictive model in which the only independent variable is temperature. Equation 14 expands the usefulness of eq 12 to tomato samples with different initial concentration and hence different physical states.

Model Validation. The efficiency of the model proposed (eq 14) in predicting apparent bleaching rate in tomato was verified by comparing experimental values of k with those estimated by the model. Validation experiments are generally chosen arbitrarily but within the specific interval of experimental conditions considered for generating the model. For this reason, a tomato sample with 0.44 solid fraction was chosen since this concentration was set around the middle of the overall interval of concentrations examined. Tomato samples with 0.44 solid fraction were thus prepared and stored at temperatures below 0 °C. Their bleaching rates were experimentally determined and compared to those predicted by eq 14 ($E_a = 17.69$ kJ/mol, $k_o = 5.90$). Data presented in **Table 7** clearly indicate that the model proposed is able to accurately predict apparent bleaching rate of tomato on the basis of only its concentration and storage temperature.

In conclusion, results obtained in this study clearly showed the non-Arrhenius behavior of pigment bleaching in tomato derivatives at subzero temperatures. Data collected were used to identify key controlling factors, which generated prediction errors. Although it is not excluded in principle that other factors,

ignored in model development, could play an important role in certain conditions, the rate of bleaching in tomato derivatives was shown to be the resultant of the interplay of two different key controlling factors, tomato solid fraction and storage temperature. While the latter exerts both a direct effect, accounted for by the Arrhenius type relation, and an indirect effect, described by the corrective factor relevant to the local concentration of reactants, tomato concentration mainly affects the temperature dependence of bleaching by changing the apparent activation energy and preexponential factor.

It must be noted that, to study the rate of bleaching of tomato derivatives, the lag phases, whose prediction is strictly necessary to model shelf life, were not considered in this research. However, validation of the model proposed clearly indicates the utility of this mathematical instrument in assisting in shelf life decisions relevant to foods where pigment oxidation is the main factor leading to quality depletion.

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1308 *J. Agric. Food Chem.,* Vol. 54, No. 4, 2006

Manzocco et al.

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